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The Barker - Henderson prescription for obtaining spherical reference systems was tested for hard linear triatimics, hard heteronuclear dumbells, and two-component mixtures of hard dumbbells. Analytic approximations using median - like methods for molecular liquids were compared with Monte Carlo simulation data. Pertabative schemes and integral equation theories were compared with computer simulations for fluids at high pressures. Rules were derived for collisions between hard spheres in arbitrary dimensions in the isobaric - isoenthalpic ensemble.

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FINAL SCIENTIFIC REPORT

AFOSR GRANT 85-0014

TITLE: STATISTICAL MECHANICS OF COMPLEX MOLECULAR SYSTEMS

NOVEMBER 1, 1984 - OCTOBER 31, 1986

by

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INTRODUCTION

In the period November 1, 1984 to October 31, 1986 we have carried out statistical mechanical studies of the equation of state and structure of complex systems. This involved both computer simulations and the development of analytical approximation schemes. We also carried out comparisons of various proposed approximations with our, and others, simulations. The results are a better understanding of both the successes and limitations of presently available theories. Various improved approximations as well as novel computer simulations were carried out. This has lead to a substantial improvement in the state of the art in this field.

1. Spherical Reference Systems for Nonspherical Hard Interactions (G. O. Williams, J. L. Lebowitz and J. K. Percus)

We investigate the applicability of the median and Barker-Henderson prescriptions for obtaining spherical reference systems for three models: hard linear triatomics, hard heteronuclear dumbbells, and two-component mixtures of hard dumbbells. We propose an empirical method for determining the median potential for systems lacking a high degree of symmetry. For mixtures of hard molecules, we find that both the median and Barker-Henderson prescriptions give rise to approximately additive hard-sphere reference potentials.

(Jour. Phys. Chem., 88, 6488, 1984)

2. Limitations on the Usefulness of the Angular Median and Related Potentials

(David MacGowan, David B. Nicolaides, Joel L. Lebowitz and Chul-Kyu Choi)

The use of the angular median and related effective spherical potentials to predict thermodynamic properties of nonpolar homonuclear diatomic liquids has recently been shown to be efficient and accurate. Here we compare the results obtained from median-like methods for some other molecular liquids with simulation data. We find impressive agreement for linear triatomic molecules but results for tetrahedral molecules and for the overlap potential are very poor. The characteristic shape of potential energy frequency distributions at fixed separations is suggested as a criterion for the success or otherwise of the median potential.

(Molecular Physics, 58, 1, 131, 1986)

3. A Comparison of Perturbative Schemes and Integral Equation Theories with Computer Simulations for Fluids at High Pressures

(J. Talbot, J. L. Lebowitz, E. M. Waisman, D. Levesque and J.-J. Weis)

We test some refined perturbation and integral equations theories for predicting the equilibrium properties of spherical fluids, with nonstandard interactions at high densities and temperatures. The perturbation theories are fast and convenient to use and give good results for the thermodynamic properties, but not for the structure. The integral equations require more computer time, but yield thermodynamics and structure that are in very good agreement with simulations. In fact there appears to be no need for computer simulations of classical systems of particles interacting with spherical potentials in the fluid regime—at least away from transitions.

(J. Chem. Phys., 85(4), 1986)

4. Molecular Theory of Metastability*: An Update
(*Appendix to the article published in Studies in Statistical Mechanics VII, North-Holland (1979)

(O. Penrose and J. L. Lebowitz)

This appendix outlines new developments in the fields discussed in the article, concentrating on rigorous, or at least quantitatively testable, aspects.

(Studies in Statistical Mechanics. To appear)

5. Hard Spheres in the Isobaric-Isoenthalpic Ensemble

(Ph. de Smedt, J. Talbot and J. L. Lebowitz)

We derive the rules for collisions between hard spheres in arbitrary dimensions in the isobaric-isoenthalpic ensemble. The static and time-dependent properties of the one-dimensional hard rod system are investigated in detail, both theoretically and numerically.

(Molec. Phys., 59, 4, 625, 1986)

6. Multiatom Interactions in the fcc Ising Binary Alloy: Low-temperature Behavior and Monte Carlo Simulations

(Daniel F. Styer, Mohan K. Phani and Joel L. Lebowitz)

We investigate an Ising model of an ordering binary alloy on the face-centered-cubic lattice, such as Cu-Au. This model contains multiatom interactions on the triangles and tetrahedra of the lattice as well as the usual repulsions on the nearest-neighbor bonds. We examine the model's ground states and its low-temperature equilibrium states: There are an infinite number of the former but only a few of the latter. We also study its phase diagram using Monte Carlo simulations, which confirm the broad conclusions of previous cluster-variation-method calculations, particularly near stoichiometry. Even small triangular interactions can introduce dramatic asymmetry into the phase diagram, making it similar to those observed in real alloys.

(Phys. Rev. B, 34, 5, 1 September 1986)

7. On the Orientational Properties of Some One-Dimensional Model Systems

(J. L. Lebowitz, J. K. Percus and J. Talbot)

We obtain exact results for hard ellipsoids and other molecular shapes, whose centers are confined to a line, in the limit of long elongation.

8. Hard Spheres in the Isobaric-Isoenthalpic Ensemble

(Ph. de Smedt, J. Talbot and J. L. Lebowitz)

We derive the rules for collisions between hard spheres in arbitrary dimensions in the isobaric-isoenthalpic ensemble. The static and time-dependent properties of the one-dimensional hard rod system are investigated in detail, both theoretically and numerically. (Molec. Phys., 59, 4, 625, 1986)

9. Effective Spherical Potentials for the Thermodynamics of Homonuclear Diatomic Lennard-Jones Liquids

(David MacGowan)

The predictions of several effective spherical potentials for thermodynamic properties of symmetric diatomic Lennard-Jones molecules are examined. The effective potentials are obtained by splitting the molecular potential in various ways followed by adding the separate angular medians of the two parts. Luckily, the best results are obtained when each site-site interaction is divided into its individual power law terms. It is therefore possible to obtain quite accurate thermodynamic properties over a continuous range of elongations using linear combinations of just two spherical potentials for which accurate analytic fitting functions are provided.

(J. Chem. Phys. 81(7), 1984)

10. **Angular Correlations in Dense Hot Diatomic Fluids**
(David MacGowan, J. D. Johnson and M. S. Shaw)

Molecular dynamics (MD) simulation data for rigid diatomic models of N_2 and CO_2 under conditions of extremely high density and temperature are analyzed for static correlation functions. The results show some significant qualitative differences from those for diatomic fluids at normal densities and temperatures (i.e., near the triple point). For a single thermodynamic state of N_2, the radial distribution functions (RDFs) of the (spherical) RAM and median potentials are found, also by MD. Whereas the median gives good thermodynamic results and poor centers correlation functions, RAM produces just the opposite. Thus no explanation in terms of distribution functions is found for the success of the median for thermodynamics although an empirical correlation is found between the breakdown of median thermodynamics for CO_2 and a distinctive feature of the molecular correlation functions.

(J. Chem. Phys. 82(8), 1985)

11. Do Interactions Raise or Lower a Percolation Threshold?
(A. L. R. Bug, S. A. Safran, Gary S. Grest and Itzhak Webman)

A Monte Carlo study of spherical particles shows that increased interaction strength may either raise or lower the volume fraction required for percolation. The sense of the change depends on the distance at which two particles are considered connected, the dimensionality, and the proximity to the critical temperature. An on-lattice simulation supports the continuum result.

(Phys. Rev. Letts., 55, 18, 1896, 25 October 1985)

12. The Planar Dumbbell Fluid

(J. Talbot and D. J. Tildesley)

The thermodynamic and structural properties of the planar dumbbell fluid are examined. The Reference Interaction Site Model (RISM) theory in two dimensions is used to calculate the site-site radial distribution functions for a range of elongations and densities. The results are compared with Monte Carlo simulations. This theory also provides a route to the thermodynamic properties. Scaled particle theory, the y expansion of Barboy and Gelbart, and a median potential are also applied to the problem of predicting the thermodynamic properties. The relative merits of the theories are discussed.

(Jour. Chem. Phys., 83(12), 1985)

13. Statistical Mechanics of Hard Ellipsoids. I. Overlap Algorithm and the Contact Function

(John W. Perram and M. S. Wertheim)

A contact function for two arbitrary ellipsoids is derived. The numerical value of the contact function is less than 1 if they overlap, and greater than 1 if they do not. This extends previous work by Vieillard-Baron, who derived an overlap criterion for spheroids without use of a contact function. The equivalence of the two criteria has been checked by extensive numerical test with spheroids. It is shown that the use of the contact function greatly facilitates the calculation of the pressure in Monte Carlo simulations.

(Jour. Computational Phys., 58, 3, May 15, 1985)

14. Sphericalized Molecular Interactions. A Review
(J. K. Percus)

The possibility of representing the classical thermodynamics of a molecular fluid by that of a suitable simple fluid is studied, both for various hard core molecular interactions and for site-site Lennard-Jones interactions. The median potential, density and temperature independent, is highly effective for all cases considered, and in the case of hard interactions is indistinguishable from the Barker-Henderson prescription.
(Annals of the New York Academy of Sciences, 452, 67, 1985)